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The use of binary mixtures of 1-butyl-1-methylpyrrolidinium bis{(trifluoromethyl)sulfonyl}imide and aliphatic nitrile solvents as electrolyte for supercapacitors

Christoph Schütter^{a,b,d}, Alex R. Neale^c, Patrick Wilde^c, Peter Goodrich^c,
Christopher Hardacre^c, Stefano Passerini^{d,e}, Johan Jacquemin^c, Andrea Balducci^{a,b,d,*}

^a Institute for Technical Chemistry and Environmental Chemistry, Friedrich-Schiller-University Jena, Philosophenweg 7a, 07743 Jena, Germany

^b Center for Energy and Environmental Chemistry Jena (CEEC Jena), Friedrich-Schiller-University Jena, Philosophenweg 7a, 07743 Jena, Germany

^c School of Chemistry and Chemical Engineering, David Keir Building, Queen's University Belfast, Belfast, Northern Ireland, BT9 5AG, United Kingdom

^d Helmholtz Institute Ulm, Helmholtzstraße 11, 89081 Ulm, Germany

^e Karlsruhe Institute of Technology (KIT), PO Box 3640, 76021 Karlsruhe, Germany

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ABSTRACT

The development of high voltage electrolytes is one of the key aspects for increasing both energy and power density of electrochemical double layer capacitors (EDLCs). The usage of blends of ionic liquids and organic solvents has been considered as a feasible strategy since these electrolytes combine high usable voltages and good transport properties at the same time. In this work, the ionic liquid 1-butyl-1-methylpyrrolidinium bis{(trifluoromethyl)sulfonyl}imide ([Pyr₁₄][TFSI]) was mixed with two nitrile-based organic solvents, namely butyronitrile and adiponitrile, and the resulting blends were investigated regarding their usage in electrochemical double layer capacitors. Both blends have a high electrochemical stability, which was confirmed by prolonged float tests at 3.2 V, as well as, good transport properties. In fact, the butyronitrile blend reaches a conductivity of 17.14 mS·cm⁻¹ and a viscosity of 2.46 mPa·s at 20 °C, which is better than the state-of-the-art electrolyte (1 mol·dm⁻³ of tetraethylammonium tetrafluoroborate in propylene carbonate).

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1. Introduction

In the field of electrochemical storage devices electrochemical double layer capacitors (EDLCs), which are also known as supercapacitors, are typically the desired technology when confronted with applications where fast delivery and/or uptake of energy is needed [1–4]. The energy in EDLCs is stored in a double layer, which is formed during charging by separating the positively and negatively charged ions in the electrolyte and adsorbing them at the electrodes' surface with the opposite charge. This charging process is much faster than the redox reactions taking place in battery systems leading to charging and discharging times in the order of seconds, an excellent cycle life (>500,000 cycles) and high power outputs (10 kW·kg⁻¹) [1–4].

Typically, activated carbons (ACs) are nowadays used as active materials, while electrolytes usually consist of organic solvents like propylene carbonate (PC) or acetonitrile (ACN) and tetraalkylammonium-salts like tetraethylammonium tetrafluoroborate ([Et₄N][BF₄]) [5–8]. EDLCs using this setup of organic electrolyte and AC-based electrodes deliver an energy in the order of 5 Wh·kg⁻¹ and a maximum usable voltage of 2.7 V–2.8 V [3,8,9]. Since the energy stored, *E*, in EDLCs is defined by the expression, *E* = 0.5·*C*·*V*², where *C* and *V* represent the capacitance and the operative voltage of the device, respectively, it is evident that an increase in the EDLCs' usable voltage will have a great impact on the EDLCs' supplied energy, which in turn would allow their usage in wider range of applications and, therefore, increase the market size of EDLCs [7].

The limiting factor of the maximum usable voltage in EDLCs is the electrochemical stability of the electrolyte [2]. One group of electrolytic materials that offers a wider range of electrochemical stability compared to the commonly used organic solvents based electrolytes, is the group of ionic liquids (ILs) [2]. ILs offer a unique set of properties which make them interesting for many energy

* Corresponding author at: Institute for Technical Chemistry and Environmental Chemistry, Friedrich-Schiller-University Jena, Philosophenweg 7a, 07743 Jena, Germany.

E-mail address: andrea.balducci@uni-jena.de (A. Balducci).

applications, i.e. lithium and sodium ion batteries [10–12], EDLCs [2,13,14], dye sensitized solar cells [15–17], solar thermal collectors [18,19], actuators [20,21], fuel cells [22,23], thermoelectric cells [24,25] and water splitting [26,27], as well as other applications like CO₂ capture [28], material synthesis [29–31] or pharmaceuticals [31]. The interest in ILs for electrochemical applications primarily stems from the mentioned high electrochemical stability, which can be as high as 6 V [32]. In EDLCs, the high electrochemical stability of ILs translates into a maximum usable voltage for the final device as high as 3.2 V–3.5 V, affording an increase in energy density when compared to organic solvent based electrolytes [13]. Additionally, ILs are in general non-flammable and their vapor pressure is negligible, which has the potential to create safer devices compared to the usage of electrolytes based on volatile solvents like ACN. However, there are also some disadvantages regarding the usage of ILs: They are typically more cost-intensive than organic solvents and their typically high viscosity and low conductivity lead to an increased resistance of the device, which limits the power output of EDLCs [33]. However, high power EDLCs based on ILs with low relaxation time constants have been reported, showing that this limitation can be overcome [34]. Researching the processes taking place at the electrode-IL-interface appears to be a crucial step for tackling this issue [35–38].

Another approach to overcome the issues of low transport properties of neat ILs is the use of blends with organic solvents. Popular organic solvents used for the preparation of blends are PC [39–43], γ -butyrolactone (GBL) [42–45] and ACN [41–43,46], but also other solvents were used, i.e. adiponitrile (ADN) [47] or methoxypropionitrile [48]. Another approach for improving the performance of ILs is the use of eutectic mixtures [49,50].

Work done by Krause *et al.* has shown that mixtures of 1-butyl-1-methylpyrrolidinium bis((trifluoromethyl)sulfonyl)imide ([Pyrr₁₄][TFSI]) and PC exhibit higher conductivity and lower viscosity at 25 °C (10.3 mS·cm⁻¹ and 5.6 mPa·s, respectively) compared to the neat [Pyrr₁₄][TFSI] (2.6 mS·cm⁻¹ and 62 mPa·s, respectively), while still keeping an operative voltage as high as 3.5 V [39].

Dagousset *et al.* found a similar behavior using mixtures of GBL and different ILs, namely, [Pyrr₁₄][TFSI], 1-propyl-1-methylpyrrolidinium bis(fluorosulfonyl)imide [Pyrr₁₃][FSI] and 1-ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide [EMIM][TFSI] [45]. Besides improving both conductivity and viscosity at room temperature, also the low temperature behaviour was improved down to temperatures as low as -50 °C, possibly enabling low temperature applications.

Ruiz *et al.* explored the combination of [Pyrr₁₄][TFSI] with different carbonate and nitrile based solvents in order to assess the physical and electrochemical properties of these mixtures showing that transport properties of the IL may be drastically improved with the addition of solvent [41]. For example, the conductivity could be increased up to 45 mS·cm⁻¹ (measured at 25 °C) with a blend of [Pyrr₁₄][TFSI] and ACN [41]. However, while electrochemical stability windows from 4.19 V up to 5.90 V were reported for the different blends, EDLC testing was only performed using a maximum voltage of 2.5 V; possibly not exploiting the electrochemical stability to its full capability.

In the following we report about the use of binary mixtures of nitrile-based solvents (butyronitrile, adiponitrile) and an IL ([Pyrr₁₄][TFSI]) as possible electrolytes for EDLC application. Starting with the evaluation of the transport properties (conductivity and viscosity), all important aspects for their implementation as EDLC electrolyte are investigated, including the electrochemical stability window, the maximum operative voltage, as well as, full cell tests to test their electrochemical stability in both short and long term measurements.

2. Experimental

First of all, the used materials, adiponitrile (ADN, Sigma Aldrich, 99 %), butyronitrile (BTN, Sigma Aldrich, ≥ 99 %) and 1-butyl-1-methylpyrrolidinium bis((trifluoromethyl)sulfonyl)imide ([Pyrr₁₄][TFSI], IoLiTec, 99.5 %), were dried until their water content was below 20 ppm, as measured by Karl-Fischer technique. Both ADN and BTN were dried and stored over molecular sieve (3 Å), whereas [Pyrr₁₄][TFSI] was dried under vacuum (*ca.* 10⁻³ mbar) at 100 °C. The storing of the liquids, as well as the preparation of the electrolytes, were conducted in a dry room (H₂O < 20 ppm). The IL, [Pyrr₁₄][TFSI], was added to each nitrile until a molar fraction (*x*) of 0.14 and 0.29 was reached in BTN and ADN, respectively.

The ionic conductivity of the electrolytes and the viscosity were measured as indicated elsewhere [51]. In short, a sealed glass conductivity cell with platinized Pt electrodes was filled with a 0.01 mol·dm⁻³ aqueous solution of KCl (VWR) of known conductivity to determine its cell constant. Afterwards, the conductivity for the electrolytes was determined in the range extending from -30 °C to 80 °C. The determination of the conductivity was done by performing impedance measurements using a Solartron model 1260 Impedance coupled with a potentiostat/galvanostat 273A PAR. The estimated maximum error of the conductivity values is 5%. Regarding the viscosity, an Anton Paar Modular Compact MCR 102 Rheometer (measurement uncertainty: $\pm 0.25\%$) was used, measuring in the same temperature range of -30 °C to 80 °C (± 0.2 °C) as the conductivity.

Composite AC-based electrodes were prepared as reported previously [52]. The prepared electrodes had a final composition of 90 % active material (activated carbon, DLC Super 30, Norit), 5 % conductive additive (carbon black, SuperC65, Imerys) and 5 % binder (sodiumcarboxymethylcellulose, CMC, Walocell CRT 2000, Dow Wolff Cellulosics) with an average mass loading of the active material of 4.6 mg·cm⁻². Additionally, free standing electrodes with high mass loadings (30 mg·cm⁻²) were prepared. For these electrodes the same AC and conductive additive as for the composite electrodes were used, but the binder was replaced by polytetrafluoroethylene (PTFE, Sigma Aldrich, 60% aqueous dispersion). The final composition was 85:10:5 (activated carbon: carbon black: binder) in this case. All components were dispersed in an excess amount of ethanol and the dispersion was stirred at elevated temperatures until the slurry became a highly viscous, dough-like mass. This mass was put onto a glass plate and rolled out several times before punching out disks with a diameter of 12 mm (area = 1.13 cm²). The obtained electrodes were dried in an oven (ED 115, Binder) set to 80 °C, before drying them for 24 h under vacuum at 180 °C to remove any residual water.

For measuring the electrochemical properties of the electrolytes, Swagelok[®]-type cells were used, which were assembled in a glove-box under argon atmosphere, with oxygen and water contents below 1 ppm. As measuring devices, a Solartron model 1287A potentiostat and a VMP multichannel potentiostatic-galvanostatic system (Biologic Science Instruments), both connected to climatic chambers set to 20 °C (KBF 115 Binder), were utilized.

The measurements for the electrochemical stability window (ESW) and the operative voltage were performed using a three-electrode setup, in which a silver-wire was used as a quasi-reference electrode and a heavy, self-standing AC electrode was used as counter electrode. As working electrode, a platinum microelectrode (embedded in PEEK; active area = 0.79 mm²) was employed for the determination of the ESW and an AC-based composite electrode was utilized for the determination of the operative voltage. In both cases, a Whatman GF/D glass microfiber filter (675 μ m thickness, 13 mm diameter), drenched with 150 μ L of electrolyte, was used as separator.

The ESW was determined by linear sweep voltammetry (LSV) at $1 \text{ mV} \cdot \text{s}^{-1}$ using the Solartron controlled by Corrware[®] software. Starting from the open circuit potential (OCP), the cell potential was scanned towards more positive (anodic limit) or more negative (cathodic) limits until a strong current response, indicating the decomposition of the electrolytes, was detected.

The operative voltages of devices using the considered electrolytes were identified by cyclic voltammetry applying a scan rate of $5 \text{ mV} \cdot \text{s}^{-1}$ using the VMP workstation. The cell potential was scanned from OCP to a final potential of $0.8 \text{ V}/-0.8 \text{ V}$ vs. OCP, which was afterwards increased/decreased stepwise by 0.1 V , until the efficiency of the CV cycle dropped below 99 %.

With knowledge about the ESW and the operative voltage of the electrolytes, full cell testing was performed in a two-electrode setup using $100 \mu\text{L}$ of electrolyte by conducting cyclic voltammetry (CV) measurements and galvanostatic charge-discharge cycling. Due to the asymmetric voltage excursion of the electrolytes, the cells were balanced using electrodes with different electrode masses (m) based on the expression $C^+ \cdot m^+ \cdot \Delta V^+ = C^- \cdot m^- \cdot \Delta V^-$ using the values of specific capacitance (C) and voltage excursion (ΔV) revealed by the operative voltage test [53].

CV measurements were conducted with varying scan rates of 5, 20, 50, 100 and $200 \text{ mV} \cdot \text{s}^{-1}$. The specific capacitances reported for the CV measurements refer to the value, which was achieved at the half of the maximum voltage and were calculated using the total active mass of both electrodes.

Cycling experiments were performed by applying current densities of 0.5, 1, 2, 5 and $10 \text{ A} \cdot \text{g}^{-1}$ for 1000 cycles each. The Coulombic efficiency (η), equivalent series resistance (ESR), specific capacitance of the total active material (C), average power (P) and average energy (E) were calculated as before [39,52].

In order to assess the stability of the investigated electrolytes, float tests were carried out, keeping the EDLCs charged at their maximum voltage for a prolonged time. In detail, the cells were kept at their maximum voltage for 20 h, followed by a short cycling test of 50 cycles and impedance measurements, in order to determine changes in specific capacitance and ESR (based on the 50th cycle). This sequence was repeated 25 times for a total of 500 h of float test. Cycling during this test was performed by applying a current density of $1 \text{ A} \cdot \text{g}^{-1}$ with the maximum voltage matching the voltage during voltage hold. The impedance spectra were recorded with a 5 mV ac perturbation in the frequency region from 500 kHz to 10 mHz.

3. Results and discussion

Blends for an IL molar fraction ($x[\text{Pyrr}_{14}][\text{TFSI}]$) of 0.14 and 0.29 in BTN and ADN, respectively, have been identified as interesting electrolytes for EDLCs (detailed information about the chemical-physical properties of blends with different ionic liquid/solvent ratios are available elsewhere) [54]. These particular compositions are further characterized in this work and referred to as the

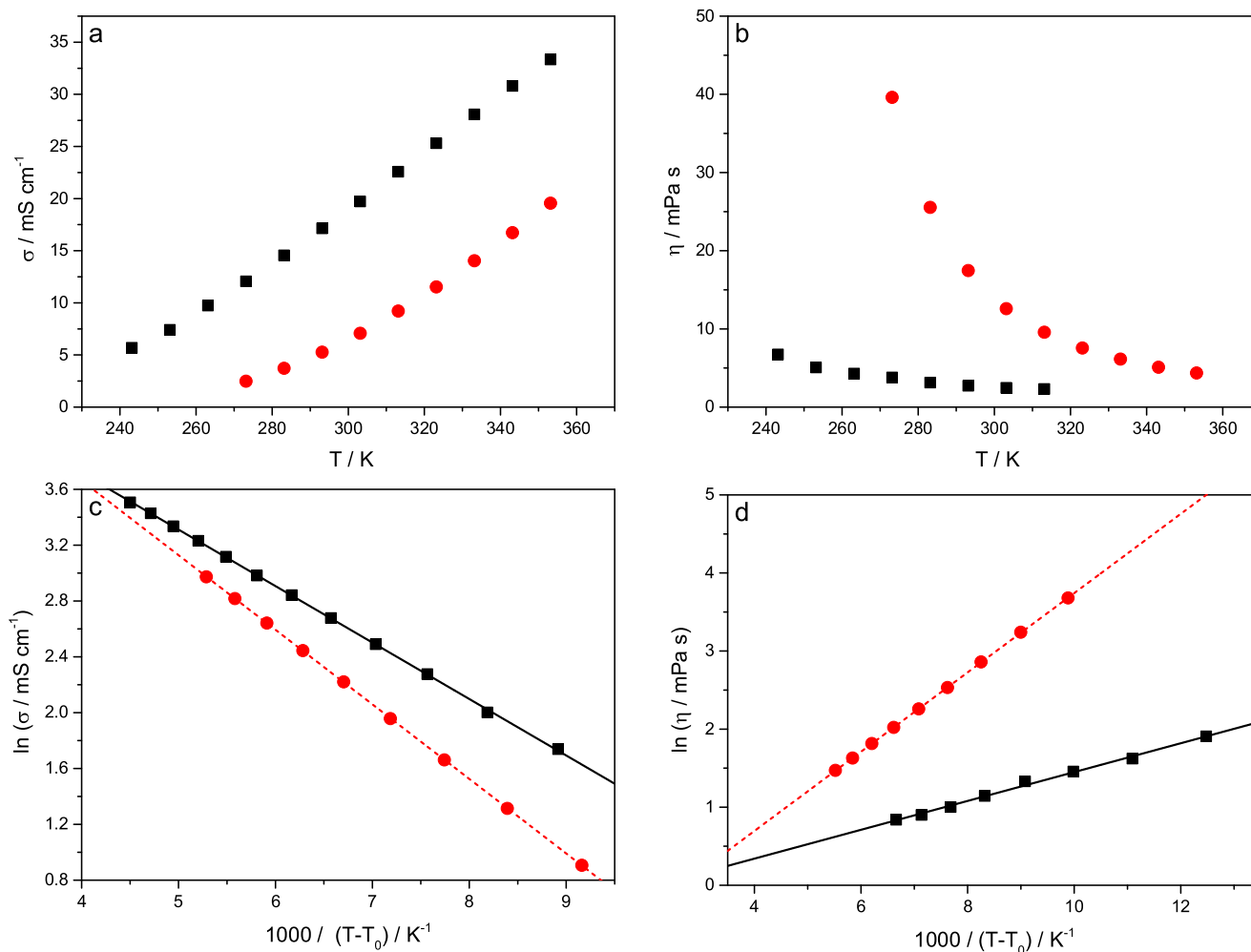


Fig. 1. (a) Conductivity, σ , and (b) viscosity, η , of the investigated blends, BTN/[Pyrr₁₄][TFSI] (■) and ADN/[Pyrr₁₄][TFSI] (●), in the temperature range of -30°C to 80°C with the corresponding VTF plots (c, d).

BTN-blend and the ADN-blend for the binary mixtures containing butyronitrile and adiponitrile, respectively.

The conductivity and viscosity were investigated in a temperature range of $-30\text{ }^{\circ}\text{C}$ to $80\text{ }^{\circ}\text{C}$ (Fig. 1). For the ADN-based electrolyte, no conductivity or viscosity was determined for temperatures below $0\text{ }^{\circ}\text{C}$, since the melting point of this blend is $-12\text{ }^{\circ}\text{C}$ as revealed by DSC measurements [54]. For the BTN-based electrolyte no viscosity was determined for temperatures above $40\text{ }^{\circ}\text{C}$, due to the high vapor pressure of BTN and, therefore, accelerated evaporation of the nitrile at higher temperatures. It is obvious that the BTN-based electrolyte has the better transport properties in comparison with the ADN based electrolyte, since the conductivity is considerably higher and the viscosity considerably lower over the whole temperature range. For example, at $20\text{ }^{\circ}\text{C}$ the ADN blend has a conductivity and viscosity of $5.27\text{ mS}\cdot\text{cm}^{-1}$ and $17.45\text{ mPa}\cdot\text{s}$, whereas the BTN reaches a conductivity of $17.14\text{ mS}\cdot\text{cm}^{-1}$ and a viscosity of $2.46\text{ mPa}\cdot\text{s}$. This observation is primarily the result of the lower viscosity of the neat BTN solvent ($0.55\text{ mPa}\cdot\text{s}$ at $25\text{ }^{\circ}\text{C}$) [55] relative to the neat ADN solvent ($5.74\text{ mPa}\cdot\text{s}$ at $25\text{ }^{\circ}\text{C}$) [47]. The BTN/[Pyrr₁₄][TFSI] blend was already considered in literature and the reported results of conductivity and viscosity are quite similar ($20\text{ mS}\cdot\text{cm}^{-1}$ and $2.3\text{ mPa}\cdot\text{s}$ at $25\text{ }^{\circ}\text{C}$, respectively) for a mixture using 57 wt% BTN [41]. The difference in conductivity and viscosity can be explained by the higher temperature and slightly higher amount of BTN (57 % compared to 50 %), which increases the transport properties. The state-of-the-art electrolytes, including $1\text{ mol}\cdot\text{dm}^{-3}$ [Et₄N][BF₄] in ACN or $1\text{ mol}\cdot\text{dm}^{-3}$ [Et₄N][BF₄] in PC, exhibit conductivities and viscosities of $55\text{ mS}\cdot\text{cm}^{-1}/0.6\text{ mPa}\cdot\text{s}$ ($25\text{ }^{\circ}\text{C}$) and $13\text{ mS}\cdot\text{cm}^{-1}/2.6\text{ mPa}\cdot\text{s}$ ($20\text{ }^{\circ}\text{C}$), respectively [56,57]. By comparing these values with those reported herein, it is clear that the nitrile/[Pyrr₁₄][TFSI] blends reported in this work cannot compete with ACN-based electrolyte. However, in comparison with the $1\text{ mol}\cdot\text{dm}^{-3}$ [Et₄N][BF₄] in PC electrolyte, the BTN/[Pyrr₁₄][TFSI] blend exhibits a higher conductivity and lower viscosity. In our recent work, we reported the use of different nitriles as electrolytes using [Et₄N][BF₄] as conductive salt [58]. Herein, a solution of $0.7\text{ mol}\cdot\text{dm}^{-3}$ [Et₄N][BF₄] in ADN displays a conductivity and viscosity of $3.5\text{ mS}\cdot\text{cm}^{-1}$ and $9.5\text{ mPa}\cdot\text{s}$ at $20\text{ }^{\circ}\text{C}$. In comparison, the ADN/[Pyrr₁₄][TFSI] blend reported in this work has a higher conductivity ($5.27\text{ mS}\cdot\text{cm}^{-1}$ at $20\text{ }^{\circ}\text{C}$), but also a higher viscosity ($17.45\text{ mPa}\cdot\text{s}$ at $20\text{ }^{\circ}\text{C}$). Therefore, the higher concentration of [Pyrr₁₄][TFSI] in ADN ($1.7\text{ mol}\cdot\text{dm}^{-3}$) seems to have a positive effect on the conductivity, but a negative one on the viscosity, which could be both related to the higher ion concentration of [Pyrr₁₄][TFSI] in the solution. However, to be certain about this point, solutions of the same concentrations should be measured and compared to exclude effects of different concentrations.

As seen in Fig. 1c and d, the temperature dependence of both conductivity and viscosity could be well described by the Vogel-Tammann-Fulcher (VTF) equations

$$\sigma = \sigma_0 \exp[-B_\sigma / (T - T_{0,\sigma})] \quad (1)$$

$$\eta = \eta_0 \exp[B_\eta / (T - T_{0,\eta})] \quad (2)$$

where σ_0 and η_0 are the limiting conductivity and viscosity, respectively, and B_σ/B_η and $T_{0,\sigma}/T_{0,\eta}$ are fitting parameters related

to the pseudo-activation energy and glass transition temperature, respectively. The VTF equation is commonly used to describe the temperature-viscosity relationship in glassy-forming liquids, such as ILs, which typically do not follow Arrhenius-type dependence. The VTF fitting parameters are reported in Table 1. For ADN, the $T_{0,\sigma}$ and $T_{0,\eta}$ temperatures obtained by the conductivity and viscosity measurements are very close to each other (164 K and 172 K , respectively), whereas for BTN there is a higher difference (131 K and 163 K , respectively). Since in each case the $T_{0,\sigma}$ and $T_{0,\eta}$ fitting parameters are expected to be the same, the values for ADN fit quite well, whereas for BTN, there is a difference of 32 K between $T_{0,\sigma}$ and $T_{0,\eta}$ values, which may be related to the fact that the fit of the viscosity of BTN does not have a good coefficient of determination ($R^2 = 0.99820$). These fitting issues in turn are a result of the “open” experimental setup of the viscosity measurements (see experimental), which allows the BTN to slowly evaporate due to its high vapor pressure even for lower temperatures.

Fig. 2 compares the electrochemical stability windows (ESWs) of the investigated electrolytes. The cathodic stability of both blends is -1.80 V vs. Ag. The BTN-based blend has an anodic stability of 1.9 V vs. Ag, whereas the ADN-based blend is stable until 2.1 V vs. Ag. After this voltage, the anodic current increases only slightly until about 3.0 V vs. Ag, where there is a sharp increase in current, indicating the oxidation of the electrolyte. Since the electrochemical stability of neat [Pyrr₁₄][TFSI] is ca. 5.5 V [59,60], the stability of the blends is limited by the stability of the nitriles. Interestingly though, in combination with [Et₄N][BF₄], ADN is stable up to 3.7 V vs. Ag on the anodic side, while having a similar stability on the cathodic side (-1.85 V) [58], suggesting that the [BF₄][−] anion might be more stable than the [TFSI][−] anion in ADN.

After the determination of the ESW, the operative voltages of the electrolytes were determined via conducting 3-electrode setup CV measurements. Fig. 3 presents the obtained CV curves as well as the obtained Coulombic efficiencies. The positive and negative potential limits were defined by the highest and lowest potentials

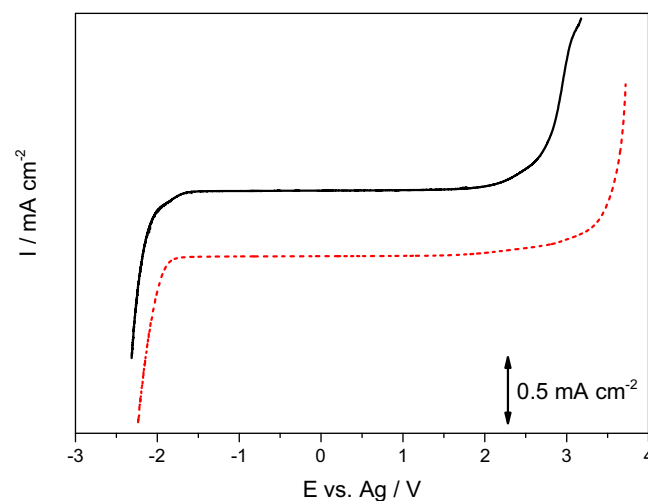


Fig. 2. Electrochemical stability windows of the BTN/[Pyrr₁₄][TFSI] (—) and ADN/[Pyrr₁₄][TFSI] (---) blends at a Pt-microelectrode.

Table 1

Molar fraction of [Pyrr₁₄][TFSI] (x_{IL}), measured flash point, conductivity (σ) and viscosity (η) at $20\text{ }^{\circ}\text{C}$, as well as, VTF fitting parameters of the nitrile blends.

Blend	x_{IL}	Flash point/ $^{\circ}\text{C}$	$\sigma/\text{mS}\cdot\text{cm}^{-1}$	$T_{0,\sigma}/\text{K}$	$\sigma_0/\text{mS}\cdot\text{cm}^{-1}$	B_σ/K	R^2	$\eta/\text{mPa}\cdot\text{s}$	$T_{0,\eta}/\text{K}$	$\eta_0/\text{mPa}\cdot\text{s}$	B_η/K	R^2
BTN/[Pyrr ₁₄][TFSI]	0.14	25	17.14	131	207.3	404.5	0.99981	2.46	163	0.667	184.8	0.99820
ADN/[Pyrr ₁₄][TFSI]	0.29	168	5.27	164	330.0	534.2	0.99999	17.45	172	0.263	507.9	0.99996

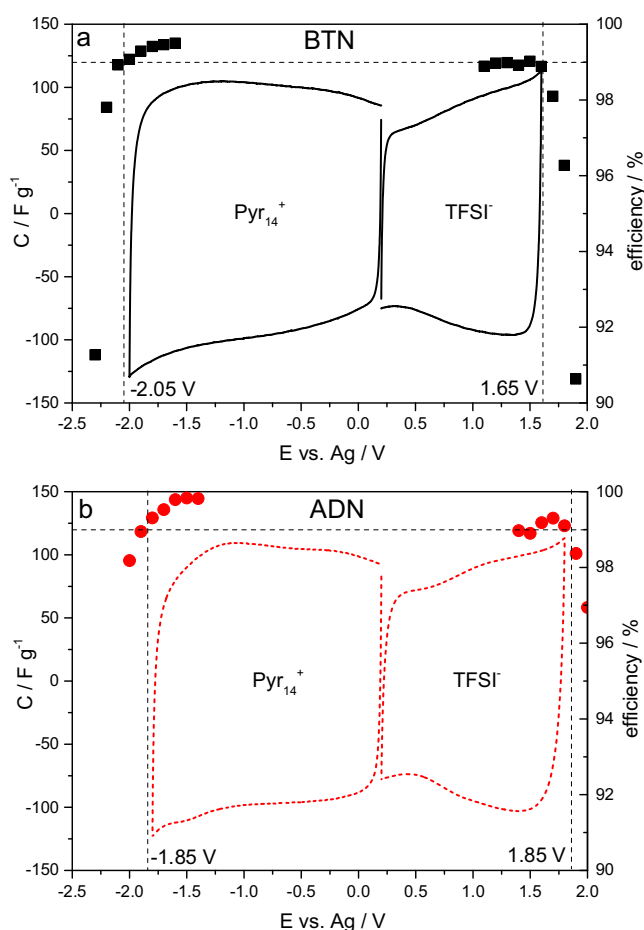


Fig. 3. Specific capacitance (line) and Coulombic efficiency (scatter) of a carbon electrode obtained from CV at 5 mV s⁻¹ for (a) BTN/[Pyr₁₄][TFSI] and (b) ADN/[Pyr₁₄][TFSI] blends. The horizontal dashed line represents a 99% threshold, the vertical dashed lines mark the potential at which the efficiency falls below 99 %.

at which the efficiency of the charge-discharge remained higher than 99 %. With this condition, the potential limits for the BTN blend were 1.65 V vs. Ag on the positive side and -2.05 V vs. Ag on the negative side. For the ADN blend, the potential limits are slightly shifted to more positive potentials (1.85 V and -1.85 V vs. Ag, respectively). Thus, the maximum operative voltage for both blends adds up to 3.7 V, the same value reported for the neat IL [39]. Therefore, the investigated nitriles do not have a negative impact on the applicable voltage for full cell EDLCs in regards to electrolyte stability. Also, the same operative voltage has been reported for an electrolyte based on ADN and 0.7 mol·dm⁻³ [Et₄N][BF₄] [58].

After the operative voltages of the different electrolytes were obtained, full cells with the two blends were assembled. Due to the different voltage excursion on the positive and negative side of the BTN blend, the masses of the electrodes were balanced in order to avoid premature electrolyte decomposition on either electrode [53]. To further decrease the chance of electrolyte decomposition, cell voltages of 3.5 V and 3.2 V were applied for full cell testing.

Fig. 4 shows the CV obtained for these full cells using a maximum cell voltage of 3.5 V (Fig. 4a and b) or 3.2 V (Fig. 4c and d). No Faradaic reactions are observed in any of the investigated electrolytes. Regardless of the [Pyr₁₄][TFSI]/nitrile blend and operating voltages employed both blends show an increase in distortion from the typical rectangular shape for the CVs for higher scan rates. At lower scan rates the difference in capacitance is negligible for the two blends, and 24 F·g⁻¹ in both BTN and ADN

were observed at 20 mV·s⁻¹, using an operative voltage of 3.5 V. For a maximum cell voltage of 3.2 V, the specific capacitance is slightly lower, displaying 23 F·g⁻¹ for both BTN and ADN. Due to the aforementioned differences in conductivity and viscosity, the ADN blend is only able to retain ca. 50 % of its initial specific capacitance upon increasing the scan rate from 5 to 200 mV·s⁻¹ whereas the BTN is able to retain ca. 80 %. In both cases the retention is independent of the maximum cell voltage employed.

To further investigate the performance of the electrolytes, galvanostatic cycling experiments were performed using current densities ranging from 0.5 A·g⁻¹ to 10 A·g⁻¹ (Fig. 5). Similar to the CV measurements, operative voltages of 3.5 V and 3.2 V were investigated. The corresponding voltage profiles for the lowest and highest current densities used are presented in Fig. 6. For all electrolytes the Coulombic efficiency is stable for all cycles and all applied current densities, reaching almost 100 %. The ESR reaches a value of ~10 Ω·cm² for BTN and ~16 Ω·cm² for ADN and remains stable upon cycling, independent of applied cell voltage. This is somewhat surprising given the differences in conductivity and viscosity for both blends; however, the higher resistance in the case of the ADN system was expected. At lower current densities the specific capacitance for both blends is almost identical, reaching ca. 21 F·g⁻¹ at a current density of 1 A·g⁻¹, which is a comparable value to other AC based EDLCs using binary mixtures of organic solvents and ILs [46,61]. However, at higher current densities, the better transport properties in conductivity and viscosity for the BTN-based blend allow for a higher retention of the capacitance. For example, at 10 A·g⁻¹ the cells using this electrolyte are still able to deliver 18 F·g⁻¹ (82 % of the capacitance at 0.5 A·g⁻¹), whereas the cell using ADN as the electrolyte solvent no longer displays any capacitive behavior at this rate. Upon cycling, a stronger decrease in the specific capacitance can be observed for the higher cell voltage of 3.5 V, especially for the ADN blend. Initially, the specific capacitance was the same at 0.5 A·g⁻¹ (22 F·g⁻¹), but after 4000 cycles the specific capacitance for the 3.2 V cell is higher than for the 3.5 V cell (16 F·g⁻¹ and 14 F·g⁻¹, respectively). The difference in capacitance loss for the different voltages is not too large (27 % at 3.2 V and 36 % at 3.5 V), it may, nevertheless, be an indication of long term stability problems.

The average energy and average power were calculated, according to reference 39, for the devices and plotted in a Ragone-like plot (Fig. 7). The mass used for the calculation refers to the sum of the active mass of both positive and negative electrodes. Also, to get a better insight into the responsiveness of the devices, the time constants τ have been calculated, as indicated by Taberna *et al.* [62], and values of 12 s for the BTN blend and 32 s for the ADN blend were found. At 1 A·g⁻¹ and a maximum cell voltage of 3.5 V the devices with the BTN blend deliver an average energy and power of 32.2 Wh·kg⁻¹ and 1.7 kW·kg⁻¹, respectively. With a maximum cell voltage of 3.2 V, these values decrease to 26.0 Wh·kg⁻¹ and 1.5 kW·kg⁻¹. Since the voltage of the cell has a strong impact on the energy and power delivered by EDLCs, a decrease in energy and power when going from 3.5 V to 3.2 V was expected. Similarly, the energy and power density for the ADN blend decreases from 23.3 Wh·kg⁻¹ and 1.4 kW·kg⁻¹, respectively (at 3.5 V) to 21.8 Wh·kg⁻¹ and 1.3 kW·kg⁻¹, respectively (at 3.2 V). For higher current densities the BTN blend clearly outperforms the ADN blend, due to its higher conductivity and lower viscosity. The values for average energy and power achieved here are very comparable to systems using similar combinations of electrode materials and other type of non-conventional electrolytes [46,61,63]. Particularly, the performance of the device containing the ADN blend appears comparable to data already reported for this type of solvent, while the performance of the device containing the BTN blend appears similar to results obtained for high voltage PC-based devices [39,56,58,61].

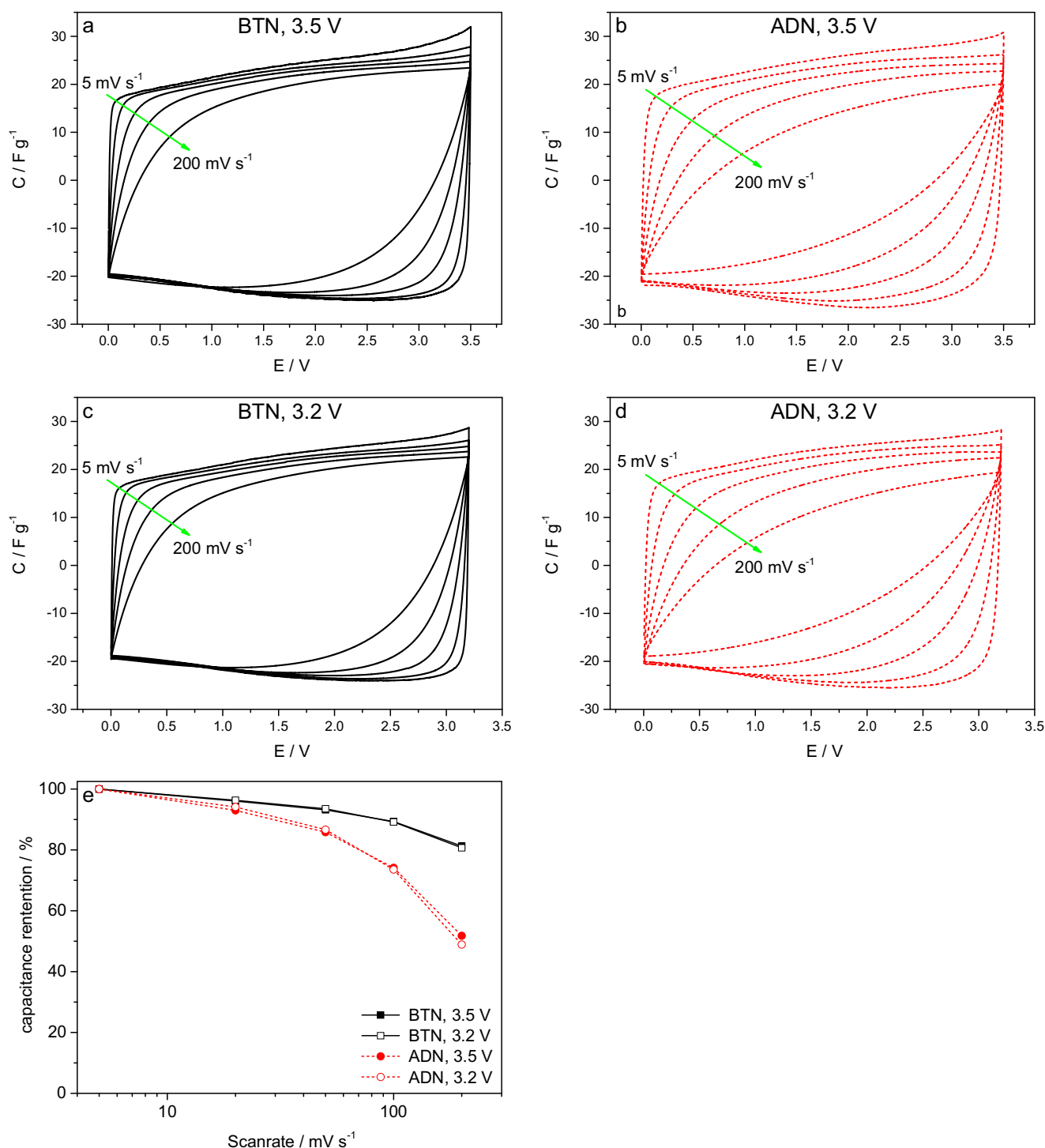


Fig. 4. Cyclic voltammograms of the investigated BTN (—) and ADN (---) blends at different maximum cell voltages of (a, b) 3.5 V and (c, d) 3.2 V. (e) Capacitance retention for the different setups.

Finally, float tests were carried out as a stress test, keeping the cells charged at their respective maximum voltage for 200 h. In intervals of 20 h, short charge/discharge steps as well impedance measurements were performed to follow the development of capacitance and ESR. As seen in Fig. 8, the stability of the electrolytes is strongly dependent on the applied voltage. Independent of the $[Pyrr_{14}][TFSI]$ /nitrile blend employed, a huge capacitance loss and ESR increase can be observed for a voltage of 3.5 V. In the corresponding Nyquist plots, semicircles can be observed in the high frequency region, which can be attributed to

contact resistance between the current collector and the carbon coating. More importantly, as the number investigated intervals of 20 h increases, the size of these semicircles also increases. These observations highlight the degradation processes taking place at a maximum voltage of 3.5 V. In comparison, when using a maximum of 3.2 V, the stability of the electrolytes is greatly increased with only a small decrease of capacitance and increase of ESR. Furthermore, the specific capacitance decreases from $21 F \cdot g^{-1}$ to $15 F \cdot g^{-1}$ and $19 F \cdot g^{-1}$ for the BTN and ADN blends, respectively, whereas the ESR increases from $17 \Omega \cdot cm^2$ to $20 \Omega \cdot cm^2$ (ADN) and

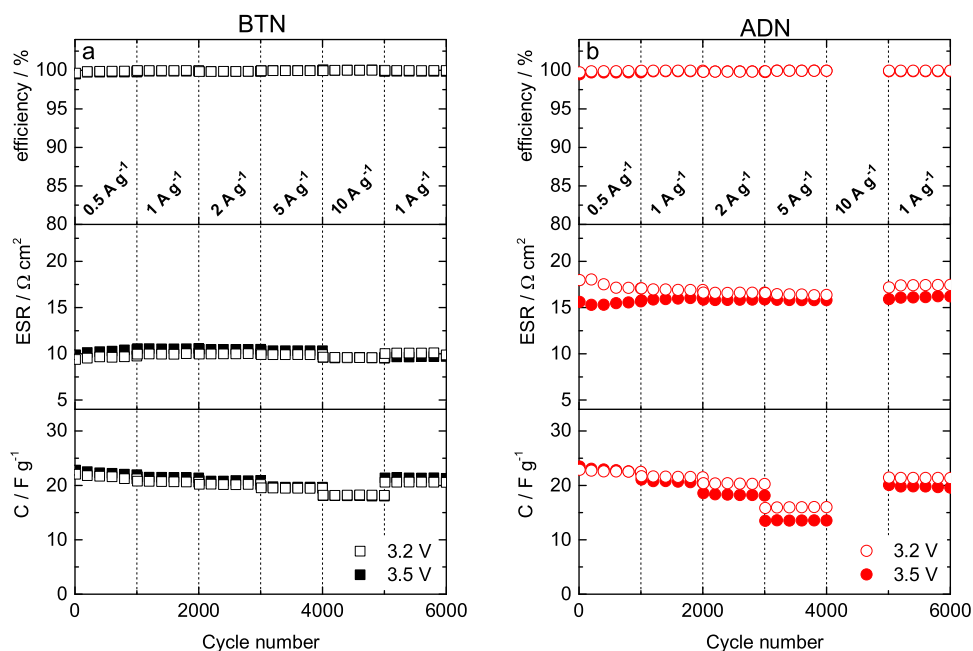


Fig. 5. Evolution of specific capacitance, ESR and Coulombic efficiency of EDLCs containing (a) the BTN blend at 3.5 (■) and 3.2 V (□) as well as (b) the ADN blend at 3.5 (●) and 3.2 V (○) using current densities from 0.5 to 10 A g⁻¹.

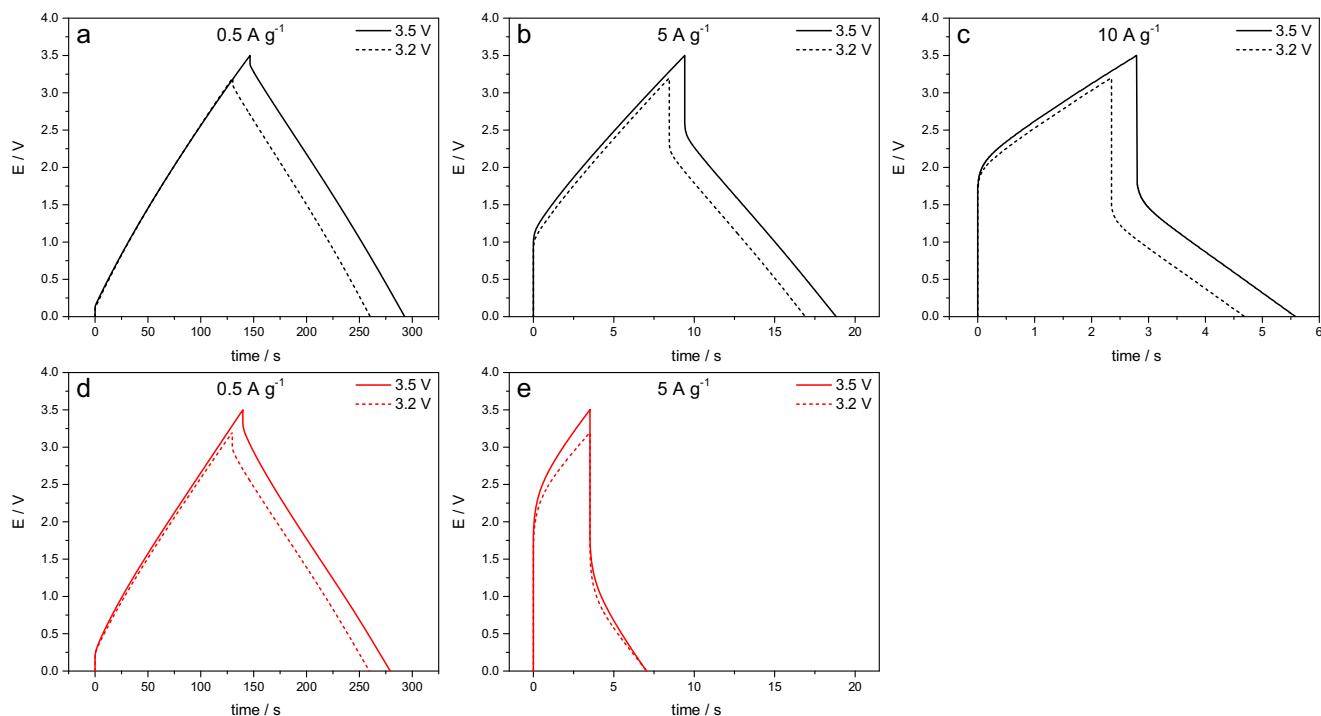


Fig. 6. Voltage profiles of the 1000th cycle of BTN (—) and ADN (---) blends at different maximum cell voltages of 3.5 V (solid line) and 3.2 V (dashed line) for current densities of (a), (d) 0.5 A g⁻¹, (b), (e) 5 A g⁻¹ and (c) 10 A g⁻¹.

from 10 Ω cm² to 15 Ω cm² (BTN). Similar to the charge-discharge tests, the corresponding Nyquist plots (Fig. 8b) of the 3.2 V cells also show only small changes in the high frequency semicircles over the course of 200 h. The stronger decrease in capacitance and increase in ESR for the BTN blends compared to the ADN blends are an indication for higher stability of the ADN based blends at the investigated voltages, although the same operative voltage was determined for both blends. It is reported that the combination of carbonate based organic solvents and the [TFSI]⁻ anion leads to

anodic dissolution of Al current collectors by forming Al-[TFSI]-complexes, which are soluble in the carbonate based organic solvents [64]. Photographs of the used electrodes after float tests (Fig. 8b) indicate that this anodic dissolution also takes place for the investigated nitrile/[Pyrr₁₄][TFSI] blends. The positive electrodes of the BTN blend have holes in them and also at the edges huge parts of the electrodes are missing, with a more significant dissolution taking place at the higher voltage of 3.5 V. In comparison, the positive electrodes of the ADN blend show no

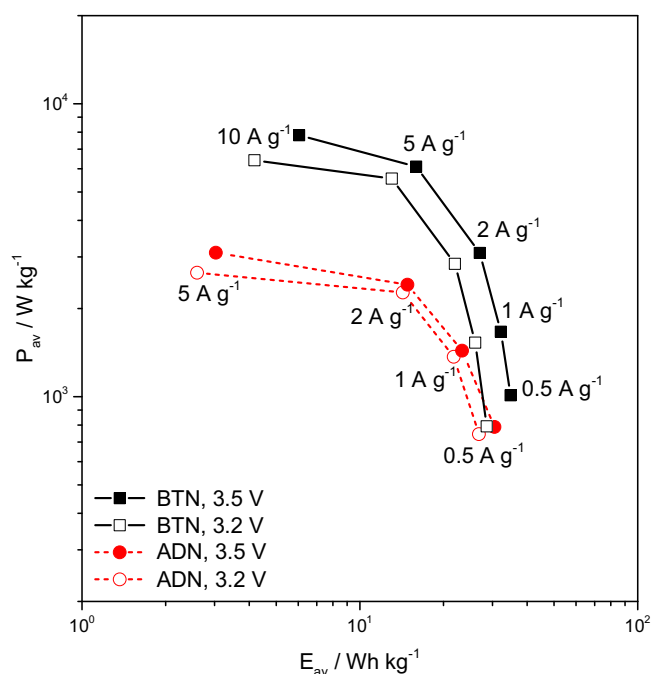


Fig. 7. Ragone plot of EDLCs containing the considered nitrile blends as electrolyte. Both average energy and power are normalized to the total mass of active materials of both electrodes.

visible holes for the same electrochemical conditions. Therefore, it is reasonable to assume that the solubility of the Al-[TFSI]-complexes might be lower in ADN compared to BTN, leading to the higher stability of the ADN blend in the float test. The lower solubility may be related to the higher viscosity of ADN; however, more investigations are necessary to completely assess the

different processes occurring in the BTN and ADN electrolyte blends.

4. Conclusion

In this manuscript we have reported about the use of blends of nitriles, namely BTN and ADN, and [Pyrr₁₄][TFSI] in EDLCs. Investigations included the determination of physical (conductivity, viscosity) and electrochemical (electrochemical stability, operative voltage, specific capacitance) properties.

Based on the results of the conductivity and viscosity measurements, the BTN blend has the superior transport properties with higher conductivity ($17.14 \text{ mS}\cdot\text{cm}^{-1}$ at 20°C) and lower viscosity ($2.46 \text{ mPa}\cdot\text{s}$ at 20°C) than the ADN blend. In fact, these values are slightly better than the commonly used organic solvent based electrolyte of $1 \text{ mol}\cdot\text{dm}^{-3}$ Et₄NBF₄ in PC ($13 \text{ mS}\cdot\text{cm}^{-1}/2.6 \text{ mPa}\cdot\text{s}$ at 25°C , respectively). By using a three-electrode configuration, the electrochemical investigations revealed a good electrochemical stability allowing a maximum operative voltage up to 3.7 V for both blends. However, while both blends show reasonable values for specific capacitance and ESR using a maximum voltage of 3.5 V , applying this voltage for prolonged time during float testing led to severe losses in specific capacitance and increases in ESR. By reducing the maximum cell voltage to 3.2 V , only small changes in specific capacitance and ESR were observed after 200 h of float testing. Cells with the ADN blend, for example, were able to still display 89% of the initial capacitance. The strong degradation of the electrochemical performance at 3.5 V was attributed to the anodic dissolution of the aluminum current collector by the [TFSI][−]-anion, however more in-depth studies are necessary to fully confirm this.

Due to their high stability with an operative voltage as high as 3.2 V and, in case of the BTN blend, similar transport properties to PC/[Et₄N][BF₄], the investigated blends surely seem to be promising alternatives to conventional electrolytes. As a matter of fact,

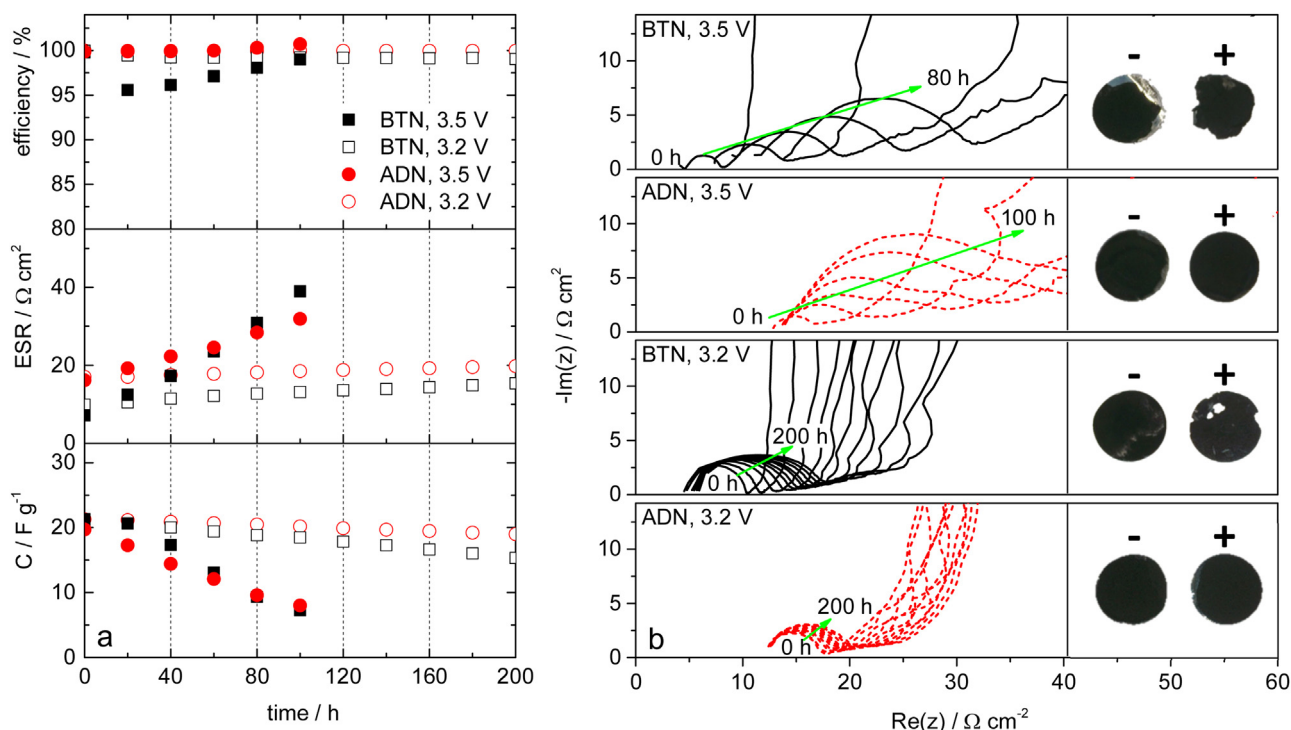


Fig. 8. (a) Evolution of specific capacitance, ESR and efficiency for 200 h float test. (b) Nyquist plots at the corresponding time intervals (20 h) and photos of the electrodes after cell disassembly.

using these electrolytes it is possible to realize EDLCs which are able to deliver energy and power values among the highest reported so far for devices containing non-conventional electrolyte [13]. These results confirm that the use of blends of organic solvent and ionic liquids represent one of the most interesting and successful strategies for the realization of advanced EDLCs.

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